Effective Macroscopic Response of a Composite with Small Deviations from Periodicity: Application to Colloidal Crystals

Sergey V. Barabash, David Stroud [a]

[a] Department of Physics, The Ohio State University, Columbus, Ohio 43210

Using the spectral approach, we analyze the effective properties of a composite which deviates slightly from periodicity. We find that, when the inclusions are randomly displaced from their equilibrium positions, the sharp resonances seen in the periodic case are broadened, and an additional branch cut appears. We use these results to analyze the effective dielectric constant of a colloidal crystal.

The spectral approach[1] has proven useful in analyzing the effective dielectric constant of a composite material. For example, it has led to the derivation of exact bounds on such effective properties[2,3], as well as to approximate calculations of effective nonlinear properties[4]; and it can be generalized to polycrystalline materials[5]. However, it has proven difficult to apply to the spectra of real systems, with the exception of a few simple cases, such as a simple cubic lattice of identical spheres[1,6].

In this paper, we achieve some progress in this direction by calculating the effect of weak disorder on a periodic arrangement of identical inclusions. Our results may prove useful in describing the effective properties of real systems such as colloidal crystals.

First we review the periodic case. Consider a system of identical inclusions (labeled by the index a). Let the spectrum of each inclusion be described by the poles $\{s_{\alpha a}\} = \{s_\alpha\}$ with the corresponding amplitudes $\{M_{\alpha a}\} = \{M_\alpha\}$, and let $Q_{\alpha a,\beta b}$ be the overlap integrals between the inclusions (see Ref. [1] for further definitions). The poles of the system are then given by the solutions of

$$(s - s_{\alpha a})A_{\alpha a} = \sum_{\beta, b \neq a} Q_{\alpha a,\beta b}A_{\beta b}, \qquad (1)$$

where the amplitude of the pole $s^{(i)}$ is

$$M^{(i)} = \sum_{\alpha a} A_{\alpha a}^{(i)} M_{\alpha a} \Big/ \sqrt{\sum_{\alpha a} |A_{\alpha a}^{(i)}|^2}. \qquad (2)$$

In the purely periodic case, Bloch theorem implies that $A_{\alpha a} = A_\alpha(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{R_a}}$, where $\mathbf{R_a}$ is the position of the inclusion a. Since $Q_{\alpha a,\beta b} = Q_{\alpha\beta}(\mathbf{R_b} - \mathbf{R_a})$, it then follows[1] that the spectrum is a system of "bands" given by

$$(s - s_\alpha)A_\alpha(\mathbf{k}) = \sum_\beta \tilde{Q}_{\alpha,\beta}(\mathbf{k})A_\beta(\mathbf{k}), \qquad (3)$$

where

$$\tilde{Q}_{\alpha\beta}(\mathbf{k}) = \sum_{b \neq a} Q_{\alpha a,\beta b}e^{-i\mathbf{k}\cdot(\mathbf{R_a}-\mathbf{R_b})}. \qquad (4)$$

For the periodic case, the entire amplitude within each band is concentrated in the $\mathbf{k} = 0$ pole:

$$M^{(i)}(\mathbf{k}) = \frac{\delta_{\mathbf{k},0}\sqrt{N}\sum_\alpha A_\alpha^{(i)}(0)M_\alpha}{\sqrt{\sum_\alpha |A_\alpha^{(i)}(0)|^2}}, \qquad (5)$$

where $N \to \infty$ is the number of inclusions in the system.

We now introduce disorder into the system by displacing the inclusions to positions

$$\mathbf{r_a} = \mathbf{R_a} + \sum_{\mathbf{k}} \mathbf{U_k} e^{i\mathbf{k}\cdot\mathbf{R_a}}. \tag{6}$$

Eq. (6) could, for example, describe a system of phonons in a colloidal crystal. Each $\mathbf{U_k}$ defines the amplitude and polarization of a phonon with wave vector $\mathbf{k}$. We will assume that all nonzero $\mathbf{U_k}$'s are of the same order of magnitude: $|\mathbf{U_k}| \sim U_{ph}$, and treat U_{ph} as a small parameter. To find the effect of such a "phononic" perturbation on the spectrum of the system, we express $A_{\alpha a}$ as

$$A_{\alpha a} = \sum_{\mathbf{k}} A_\alpha(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R_a}}, \tag{7}$$

where $\mathbf{k}$ is confined to the first Brillouin zone. Substituting (7) into (1), we find that Eqs. (3-4) should now be generalized to

$$(s - s_\alpha)A_\alpha(\mathbf{k}) = \sum_{\beta\mathbf{k}'} \tilde{Q}_{\alpha,\beta}(\mathbf{k},\mathbf{k}')A_\beta(\mathbf{k}'), \tag{8}$$

$$\tilde{Q}_{\alpha,\beta}(\mathbf{k},\mathbf{k}') = \frac{1}{N} \sum_a \sum_{b \neq a} Q_{\alpha a,\beta b}\, e^{i(\mathbf{k}'\cdot\mathbf{R_b} - \mathbf{k}\cdot\mathbf{R_a})}. \tag{9}$$

If we restrict our consideration to the correction of the lowest order in U_{ph}, we can explicitly write down the approximate expression for the position-dependent overlap integrals $Q_{\alpha a,\beta b}$:

$$
\begin{aligned}
Q_{\alpha a,\beta b} &= Q_{\alpha,\beta}(\mathbf{R_b} - \mathbf{R_a}) + \delta Q^{(1)}_{\alpha a,\beta b}; \\
\delta Q^{(1)}_{\alpha a,\beta b} &\equiv \sum_{\mathbf{k}} \mathbf{U_k} \cdot (\nabla Q_{\alpha,\beta}(\mathbf{R_b} - \mathbf{R_a})) \\
&\quad \times \left(e^{i\mathbf{k}\cdot\mathbf{R_b}} - e^{i\mathbf{k}\cdot\mathbf{R_a}} \right).
\end{aligned} \tag{10}
$$

Plugging in this expression for $\delta Q^{(1)}_{\alpha a,\beta b}$ back into Eq. (9), we obtain:

$$\tilde{Q}_{\alpha,\beta}(\mathbf{k},\mathbf{k}') = \delta_{\mathbf{k},\mathbf{k}'}\tilde{Q}_{\alpha\beta}(\mathbf{k}) + \mathbf{U_{k-k'}}\cdot\vec{\mathbf{Q}}_{\alpha,\beta}(\mathbf{k},\mathbf{k}'), \tag{11}$$

where

$$\vec{\mathbf{Q}}_{\alpha,\beta}(\mathbf{k},\mathbf{k}') = (\widetilde{\nabla Q_{\alpha,\beta}})_{\mathbf{k}} - (\widetilde{\nabla Q_{\alpha,\beta}})_{\mathbf{k}'} \tag{12}$$

and

$$(\widetilde{\nabla Q_{\alpha,\beta}})_{\mathbf{k}} = \sum_{\Delta\mathbf{R}\neq 0} [\nabla Q_{\alpha,\beta}(\Delta\mathbf{R})] \times e^{i\mathbf{k}\Delta\mathbf{R}}, \tag{13}$$

with $\Delta\mathbf{R} \equiv \mathbf{R_b} - \mathbf{R_a}$. Note that because the Fourier transforms (4) and (13) involve only discrete sums rather than continuous integrals, one cannot assume that $(\widetilde{\nabla Q_{\alpha,\beta}})_{\mathbf{k}} = \mathbf{k}\tilde{Q}_{\alpha,\beta}(\mathbf{k})$. Instead, both (4) and (13) should be evaluated directly from the known functional form of $Q_{\alpha,\beta}(\Delta\mathbf{R})$.

The Eq.(8) now takes the form

$$
\begin{aligned}
(s - s_\alpha)A_\alpha(\mathbf{k}) = \sum_\beta &\Big\{ \tilde{Q}_{\alpha,\beta}(\mathbf{k})A_\beta(\mathbf{k}) \\
&+ \sum_{\mathbf{k}'} \mathbf{U_{k-k'}}\cdot\vec{\mathbf{Q}}_{\alpha,\beta}(\mathbf{k},\mathbf{k}')A_\beta(\mathbf{k}') \Big\}.
\end{aligned} \tag{14}
$$

The solutions of this equation give the new positions of the poles and the corresponding eigenvectors. Note that unlike Eq. (3), which could be solved for each value of $\mathbf{k}$ independently, a single solution of (14) generally involves an infinite number of amplitudes $A_\alpha(\mathbf{k}')$.

We now explicitly find the solutions of (14), restricting ourselves to the case when in the purely periodic system the pole at $s_0^{(i)}(\mathbf{k}_0)$ is not degenerate. We can expand the corresponding eigenvector $A_\alpha^{(i,\mathbf{k}_0)}(\mathbf{k})$ of Eq.(14) in terms of the unperturbed eigenvectors $A_{0\alpha}^{(j)}(\mathbf{k})$ by writing

$$A_\alpha^{(i,\mathbf{k}_0)}(\mathbf{k}) = A_{0\alpha}^{(i)}(\mathbf{k})\delta_{\mathbf{k},\mathbf{k}_0} + \sum_j c_{j,\mathbf{k}}^{(i,\mathbf{k}_0)} A_{0\alpha}^{(j)}(\mathbf{k}), \tag{15}$$

where the factors $c_{j,\mathbf{k}}^{(i,\mathbf{k}_0)}$ are of the first order in phononic amplitudes. This can be done because[1] $\tilde{Q}_{\alpha,\beta}^*(\mathbf{k}) = \tilde{Q}_{\beta,\alpha}(\mathbf{k})$, and thus the different solutions $A_{0\alpha}^{(j)}(\mathbf{k})$ of (3) do form a complete set at each given value of $\mathbf{k}$; we also assume that $\sum_\alpha A_{0\alpha}^{(i)}(\mathbf{k})^* A_{0\alpha}^{(j)}(\mathbf{k}) = \delta_{i,j}$ Using the latter property and noting that

$$\sum_\beta \left[\tilde{Q}_{\alpha,\beta}(\mathbf{k}) - s_\alpha\delta_{\alpha,\beta} \right] A_{0\beta}^{(i)}(\mathbf{k})$$

$$= s_0^{(i)}(\mathbf{k})A_{0\alpha}^{(i)}(\mathbf{k}) \tag{16}$$

[cf. eq. (3)] it is straightforward to show that the first order correction to the eigenvector is given by

$$c_{j,\mathbf{k}}^{(i,\mathbf{k}_0)} = \tag{17}$$

$$\frac{\sum_{\alpha,\beta} A_{0\alpha}^{(j)}(\mathbf{k})^* \mathbf{U_{k-k_0}} \cdot \vec{\mathbf{Q}}_{\alpha,\beta}(\mathbf{k},\mathbf{k}_0) A_{0\beta}^{(i)}(\mathbf{k}_0)}{s_0^{(i)}(\mathbf{k}_0) - s_0^{(j)}(\mathbf{k})}$$

for $\mathbf{k} \neq \mathbf{k}_0$. For $\mathbf{k} = \mathbf{k}_0$, $c_{j,\mathbf{k}_0}^{(i,\mathbf{k}_0)} = 0$, reflecting the fact that the diagonal term of the perturbation is zero: $\vec{Q}_{\alpha,\beta}(\mathbf{k},\mathbf{k}) = 0$. For the same reason the position of the non-degenerate pole $s_0^{(i)}(\mathbf{k}_0)$ remains unchanged in the first order.

Next, we analyze how the amplitude of the non-degenerate pole is affected by the disorder. From (7) and (2) we get

$$M^{(i,\mathbf{k}_0)} = \frac{\sum_\alpha N M_\alpha A_\alpha^{(i,\mathbf{k}_0)}(0)}{\sqrt{N \sum_\alpha \sum_\mathbf{k} |A_\alpha^{(i,\mathbf{k}_0)}(\mathbf{k})|^2}}. \qquad (18)$$

Up to the terms of the second order, the sum in the denominator equals $\sum_\alpha |A_{0\alpha}^{(i)}(0)|^2$ which is simply unity by our our choice of orthonormal set of $A_{0\alpha}^{(i)}(\mathbf{k})$'s. Thus, in the non-degenerate case the amplitude of the pole at $\mathbf{k}_0 = 0$ remains unchanged in the first order. The amplitudes at other poles are:

$$M^{(i,\mathbf{k})} = \sqrt{N} \sum_\alpha M_\alpha \sum_j c_{j,0}^{(i,\mathbf{k})} A_{0\alpha}^{(j)}(0), \qquad (19)$$

where

$$c_{j,0}^{(i,\mathbf{k})} = \frac{\sum_{\alpha,\beta} A_{0\alpha}^{(j)}(0)^* \vec{Q}_{\alpha,\beta}(0,\mathbf{k}) \cdot \mathbf{U}_{-\mathbf{k}} A_{0\beta}^{(i)}(\mathbf{k})}{s_0^{(i)}(\mathbf{k}) - s_0^{(j)}(0)} \qquad (20)$$

Thus, for each nonzero Fourier component $\mathbf{U}_\mathbf{k}$ of the disorder, the poles $s^{(i,-\mathbf{k})}$ in each band pick up nonzero amplitude $M^{(i,-\mathbf{k})} \sim |\mathbf{U}_\mathbf{k}| \sim U_{ph}$.

What happens in the vicinity of the unperturbed poles ($\mathbf{k} = 0$)? Because $Q_{\alpha,\beta}(\Delta \mathbf{R}) \to 0$ as $\Delta \mathbf{R} \to \infty$, it follows from eq. (12) that $\vec{Q}_{\alpha,\beta}(0,\mathbf{k} \to 0) \to 0$. This, however, does not directly relate to the small-$\mathbf{k}$ behavior of $M^{(i,\mathbf{k})}$, since one also has $s_0^{(i)}(\mathbf{k} \to 0) \to s_0^{(j)}(0)$ at least for $i = j$. It is natural to expect that $s_0^{(i)}(0)$ is either at the top or at the bottom of the i-th band, in which case $s_0^{(i)}(\mathbf{k}) - s_0^{(i)}(0) \sim ak^2$ for $\mathbf{k} \to 0$, whereas the $\vec{Q}$'s are likely to follow $\vec{Q}_{\alpha,\beta}(0,\mathbf{k}) \sim \mathbf{k}$ [which would be the case if (4) and (13) were continuum Fourier transforms]. In this case, eq. (20) predicts that $c_{j,0}^{(i,\mathbf{k})} \to \infty$ as $\mathbf{k} \to 0$, which means that the expression for the first-order non-degenerate case cannot be used under these conditions. Instead, for sufficiently small values of $\mathbf{k}$ a degenerate theory

should be applied. Namely, for the states with $|\mathbf{k}| < k_c$, where k_c is chosen so that $s_0^{(i)}(\mathbf{k}_c) - s_0^{(i)}(0) \ll \sum_{\alpha,\beta} A_{0\alpha}^{(j)}(0) \vec{Q}_{\alpha,\beta}(0,\mathbf{k}_c) \cdot \mathbf{U}_{-\mathbf{k}_c} A_{0\beta}^{(i)}(\mathbf{k}_c)$, we can make the approximation $s_0^{(i)}(\mathbf{k}) \approx s_0^{(i)}(0)$. In the first order this will not change the positions of the poles, because $k_c \sim U_{ph}$ and thus $\vec{Q}_{\alpha,\beta}(0,\mathbf{k}_c) \cdot \mathbf{U}_{\mathbf{k}_c} \sim U_{ph}{}^2$. However, all the eigenvectors of the degenerate problem would contain $A_{0\beta}^{(i)}(0)$ with finite coefficients. Thus, the unperturbed weight $|M^{(i)}(0)|^2$ of the $\mathbf{k} = 0$ pole [see eq. (5)] will become distributed between all the poles $s^{(i)}(\mathbf{k})$ that correspond to $\mathbf{k} < \mathbf{k}_c$ (and such that $\mathbf{U}_{-\mathbf{k}} \neq 0$).

Consider, for example, an infinite sample in which each inclusion is randomly displaced from its original position. The sum in Eq. (6) should then be replaced by an integral over the first Brillouin zone, so that there will be a continuous density of poles with nonzero weight. The corresponding spectral function is written

$$F(s) = \int_0^1 \frac{|\mu(s')|^2}{s - s'} ds', \qquad (21)$$

where $|\mu(s)|^2$ is interpreted as a density of pole weight. In the purely periodic case (or for a finite system),

$$|\mu_0(s)|^2 = \sum_i |M^{(i)}(0)|^2 \delta\left(s - s^{(i)}(0)\right), \qquad (22)$$

so that $F(s)$ is non-analytic only at the simple poles $s^{(i)}(0)$[1]. In the presence of disorder, however,

$$\mu(s) = \mu_{peak}(s) + \mu_{band}(s), \qquad (23)$$

where $\mu_{peak}(s)$ represents the amplitudes of the discrete poles $s^{(i)}(\mathbf{k})$ which are degenerate with $s^{(i)}(0)$, while $\mu_{band}(s)$ gives the amplitude density for the rest of the band. From Eqs. (19-20), $\mu_{band}(s) \sim U_{ph}$. For the typical case discussed in the previous paragraph, the width of the peak part can be estimated by noting that $s_0^{(i)}(k_c) - s_0^{(i)}(0) \sim ak_c^2 \sim U_{ph}^2$. Therefore, we expect each δ-function entering $\mu_0(s)$ to acquire a half-width proportional to U_{ph}^2. This typical situation is illustrated in Fig. 1.
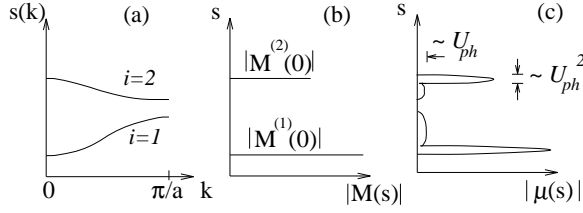
Figure 1. Schematic of (a) the "band structure" for a periodic composite (two "bands" are shown); and the corresponding pole spectrum for (b) a purely periodic, and (c) a slightly disordered system (with characteristic "phononic" amplitude U_{ph}).

For s sufficiently different from $s_0^{(i)}(0)$, $\mu_{peak}(s)$ can probably be replaced by a set of δ-functions:

$$F(s) \approx \sum_{s' \in \{s^{(i)}(0)\}} \frac{|M^{(i)}(0)|^2}{s - s'} + \int_0^1 \frac{|\mu_{band}(s')|^2}{s - s'} ds' \quad (24)$$

The second term describes the part of the spectral function which cannot be characterized purely by simple poles. Any such function can be described by a branch cut along the segment $[0, 1)$ of the real axis, as can be seen by writing the Cauchy formula for the contour encircling the branch cut infinitesimally below the real axis. For example, the effective medium approximation (EMA)[3] gives such a branch cut. While branch cut in the present case would certainly differ from the EMA one, it is quite remarkable that such a cut would appear even in a weakly disordered system.

A possible application of this work could be a colloidal crystal at some finite temperature T. The total contribution to the spectral function from the integral in (24) involves $|\mu_{band}(s')|^2$, which is determined by $\sum_{\mathbf{q}} |\mathbf{U}_{\mathbf{q}}|^2$. In a conventional crystal, the analogous sum increases linearly in T at high T and approaches constant value as $T \to 0$, and similar behavior should be observed in a colloidal crystal.

We thus suggest that in a colloidal crystal, at T such that first order corrections are adequate, the spectrum should consist of two parts: (a) electrostatic resonances at the same ratios ϵ_1/ϵ_2 pre-dicted by the theory for the periodic case [see [6] for explicit expressions for spherical inclusions], but slightly broadened by a half-width proportional to T^2; and (b) a continuous contribution from a branch cut introduced by the disorder. The latter contribution should be most prominent at negative values of ϵ_1/ϵ_2 away from the original resonances. It would be of great interest if such a spectrum could be detected in a real material, e. g., in a suspension of metal spheres in a dielectric host.

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